(2) R. C. Bingham, M. J. S. Dewar, and D. L. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307 (1975); M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *ibid.*, **97**, 1311 (1975).
(3) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, 5129 (1965).
(4) Approximate relative times for a single calculation at the MINDO and various ab initio levels are: CNDO/INDO/MINDO, 1; minimal basis STO-3G, 30; split valence basis 4-31G, 180; polarization basis 6-31G*, 1000.
(5) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(6) It must be noted that the mean error we report here, between STO-3G and experimental skeletal bond angles, is considerably smaller than that resulting from comparison of bond angles involving one or two hydrogens. See W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971); W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).
(7) Alfred P. Sloan fellow, 1974–1976.

Warren J. Hehre[7]

Department of Chemistry, University of California
Irvine, California 92664

The Mixed Valence State Based on μ-Cyanogen-bis(pentaammineruthenium)

Sir:

Binuclear complexes of ruthenium with cyanogen as the bridging ligand have been synthesized. The properties of the mixed valence complex, $[(NH_3)_5RuNCCNRu(NH_3)_5]^{5+}$, are consistent with Robin and Day[1] class III behavior, in contrast to the properties of the analogous pyrazine[2] and 4,4'-bipyridine[3] bridged mixed valence rutheniumammine complexes.

In preparing the μ-cyanogen complex a stoichiometric amount of an aqueous saturated cyanogen solution ($\sim$0.2 M) was added dropwise to $[(NH_3)_5Ru(OH_2)]^{2+}$ generated in water at pH 4. After 2 hr under an argon atmosphere, the [4+] binuclear complex was precipitated by the addition of sodium bromide or sodium tosylate. Anal. Calcd for $[(NH_3)_5RuNCCNRu(NH_3)_5]Br_4$: C, 3.2; H, 4.03; N, 22.63; Ru, 27.7. Found: C, 2.96; H, 3.93; N, 21.6; Ru, 25.8.[4]

Cyclic voltammetry at 200 mV/sec in 0.1 M HCl shows a reversible one electron oxidation of the [4+] complex at 0.71 V and a chemically irreversible (reduction wave absent) one electron oxidation at 1.25 V, both referred to NHE (cf. Figure 1). Ruthenium(III) has been shown to catalyze the hydration of nitriles to amides.[5] Stretching frequencies characteristic of amides are observed in the oxidized samples of the cyanogen complex, and the irreversibility referred to is ascribable to nitrile hydration. To avoid this reaction, DMSO was used with 0.1 M $(C_2H_5)_4NClO_4$ as the electrolyte. In this medium, the second oxidation is not observed within the anodic limits of the solvent mixture. A lower limit on the potential difference between the first and second stages of 0.80 V is set by the electrochemistry in DMSO. The lower limit for the conproportionation constant K_{con} from this difference is 10^{13}, to be compared to 1.3×10^6 for the μ-pyrazine[2,6] and $4 < K_{con} < 20$ for the μ-bipyridine system.[3]

The [4+] ion shows a band at 360 nm ($\epsilon = 6.9 \times 10^4$ M^{-1} cm^{-1}) which can reasonably be assigned to the πd–π^* transition; for the mononuclear Ru(II) complex the band is at 300 nm ($\epsilon = 2.3 \times 10^4$ M^{-1} cm^{-1}).

In common with most mixed valence complexes of this series, the [5+] ion has a near-infrared transition. Here, as is also the case with the μ-pyrazine ion,[2] the absorption maximum is virtually independent of the solvent (1430, 1480, 1450, 1450 nm in D_2O, CH_3CN, DMF, and DMSO, respectively). The band is very weak ($\epsilon = 4.1 \times 10^2$ M^{-1}
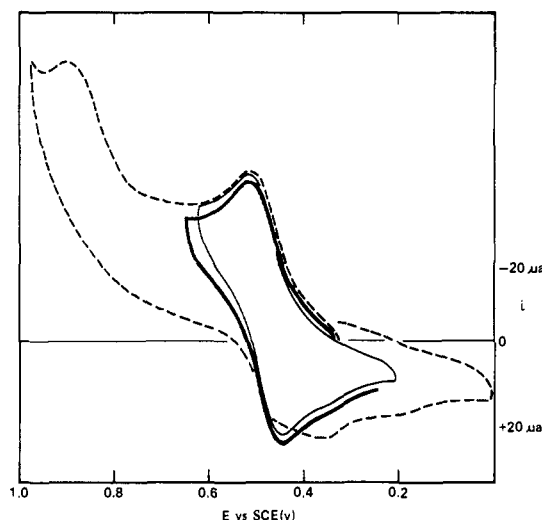

Figure 1. Cyclic voltammogram of $(NH_3)_5RuNCCNRu(NH_3)_5^{4+}$ in 0.1 M HCl at 200 mV/sec on platinum electrode. In solid curve, the anodic scan was reversed after the potential for the [4+]/[5+] couple was passed.

cm^{-1} in DMF) and is narrower than is expected on the basis of the equation given by Hush[7] ($\Delta\nu_{1/2} = 1.61$ kK compared to a calculated value of 4.0 kK).

Examination of the CN stretching frequencies sets a lower limit on the rate of electron transfer in the mixed valence species. The [4+] salts (KBr pellet) exhibit a single CN stretch at 1960 cm^{-1} in the ir and a single one in the Raman at 2185 cm^{-1}, a pattern which, apart from overtones and combination bands, the free ligand also exhibits.[8] The mononuclear complex exhibits two ir active bands at 2220 and 2090 cm^{-1}. Oxidation of the [4+] tosylate salt in DMF with $Fe(bipy)_3(ClO_4)_3$ or with Br_2 yields the [5+] complex with a single ir active band at 2210 cm^{-1}.[9] Contact of the [4+] bromide with liquid Br_2 produces a solid showing a new band at 2330 cm^{-1} in addition to the 2210-cm^{-1} band, these appearing at varying intensity ratios in different preparations. Though the stoichiometry of the reaction is difficult to control, the new frequency can reasonably be assigned to the [6+] state. Since the mixed valence species shows a single ir stretch, which differs from that of cyanogen bound only to Ru(II) (1960 cm^{-1}) or to Ru(III) (2330 cm^{-1}) electron transfer must be rapid compared to the frequency difference of 365 cm^{-1} or $>10^{13}$ sec^{-1}.

Valence delocalization in the mixed valence species is strongly suggested by the chemical behavior. By monitoring the disappearance of the near-ir transition, the rate of decomposition of the [5+] ion was determined to be 7×10^{-3} sec^{-1} in 0.12 M DCl-D_2O at 25°. The lower limit for the rate of hydration of the $(NH_3)_5RuNCCN^{3+}$ complex was found to be 10^2 sec^{-1} by cyclic voltammetry[10] and that of the [6+] μ-cyanogen species appears to be as great (an exact value for the binuclear is difficult to obtain because of the large background current). The slower rate of hydration of the mixed valence species by a factor in excess of 10^4 demonstrates that the mixed valence ion is far from showing 3+ ruthenium character. We conclude therefore that the valences are extensively delocalized in the species. The point has been made to us by Professor D. Dolphin, and quite correctly, that the interpretation of the chemical evidence is ambiguous. The decrease in rate registered for the mixed valence species may simply reflect the effect of Ru(II) on the bridging ligand. The chemical evidence is more convincing when, as in the test applied by Isied (ref 2) to the Creutz ion, nonbridging ligand positions are dealt with.

Preliminary ESCA spectra of the bromine oxidized solids have been obtained. A small peak is observed at 282.5 eV[11] which is between the observed binding energy of the Ru(II) form (281.5 eV) and that expected for the Ru(III) form (284.0 eV). (In our spectra the latter was masked by the peak attributable to carbon.)

A sufficient condition for the near-ir transitions being solvent independent is that electron transfer be rapid compared to solvent reorientation. This condition is met for the μ-cyanogen system, solvent reorientation being slow compared to the lower limit of 10^{13} sec^{-1} set on the rate of electron transfer. We suggest that for the μ-pyrazine ion, where the energy of the near-ir band is also independent of the solvent, though valence delocalization is not as complete as in the case under present consideration, electron transfer is also more rapid than is solvent reorientation, a conclusion which is supported by the averaging of some ir frequencies for the mixed valence species.[13-15]

To understand the narrowness and low intensity of the near-ir band for the μ-cyanogen system, the delocalized limit, rather than that of deep trapping, appears to offer a better first approximation in describing the state of the system. The low intensity of the near-ir transition may be a result of the electron hole being created in an xy rather than a yz or zx orbital. The ordering of the molecular orbitals in the μ-dinitrogen binuclear case, derived from the πd metal orbitals for D_{4h} symmetry[16] has been assigned $e_g(\pi^*) > e_u > b_{1u} \sim b_{2g} > e_g$. In the [5+] ion this leaves an electron vacancy in the e_u levels, with two transitions allowed $e_u \leftarrow b_{2g}$ and $e_u \leftarrow e_g$, and only the second is expected to be strong. In fact only one weak transition is observed which can reasonably be taken to correlate with an intervalence transition. To explain the observation using the orbital set proposed, this would require the highest molecular orbital to be b_{1u}. In this case only one weak transition, $b_{1u} \leftarrow e_g$, would be expected. That the b_{1u} orbital be the least stable is reasonable in the present system where the interaction of the πd and π^* orbitals is expected to be great, lowering the center of gravity of the e relative to b sets, and where, owing to the great distance of separation between the metal atoms, direct interaction of their orbitals is extremely small.

The μ-pyrazine mixed valence complex is more difficult to treat than the μ-cyanogen because it appears to be a hybrid of Robin and Day class II and class III systems.[1] Thus although electron transfer is more rapid than solvent reorientation—from the averaging of certain ir frequencies, it is more rapid than 10^{12} sec^{-1}[14]—it is not so rapid that Ru(II)-Ru(III) character has been substantially altered in the mixed valence species. It does now seem probable, however, that contrary to earlier claims,[2] the energy of the near-ir band is not related in a simple way to the Franck-Condon barrier for electron transfer. The properties of the band are rather akin to those registered for the μ-cyanogen system.

To our knowledge, the [4+] species herein described is the first cyanogen complex to have been prepared and characterized. Of more general significance is the implication of our results that averaging of valences between transition metal ions, which is common when there are metal-metal bonds or when a single atom intervenes, can take place also over large distances through suitable conjugated bond systems.

References and Notes

(1) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10**, 247 (1967).
(2) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973).
(3) G. M. Tom, C. Creutz, and H. Taube, *J. Am. Chem. Soc.*, **96**, 7827 (1974).
(4) Elemental microanalysis performed by Stanford Microanalytic Laboratory, Stanford, Calif. Ru analysis was by residue.
(5) S. E. Diamond and H. Taube, *J. Chem. Soc., Chem. Commun.*, 622 (1974); S. E. Diamond, B. Grant, G. M. Tom, and H. Taube, *Tetrahedron Lett.*, 4025 (1974).
(6) H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11**, 1460 (1972).
(7) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967).
(8) C. R. Bailey and S. C. Carson, *J. Chem. Phys.*, **7**, 859 (1939).
(9) Though oxidation of [4+] to [5+] in solution can be made quantitative, we have not obtained pure samples of a [5+] solid by this means. Oxidation with liquid Br$_2$ produces mixtures which show the 1965, 2210, 2330 cm^{-1} frequencies in varying amounts, depending among other factors on the time of contact.
(10) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(11) References to C_{1s} = 284.00 eV. For Ru(II) in the μ-pyrazine-pentaammine[12] species and in μ-4,4′-bipyrine-bis(*trans*-tetraammineisonicotinamideruthenium(II)) 280.2 and 279.6 eV, respectively, have been observed, while for the corresponding [3,3] species 283.1 and 283.1 eV are observed.
(12) P. H. Citrin, *J. Am. Chem. Soc.*, **95**, 6472 (1973).
(13) Work in progress.
(14) C. Creutz, Ph.D. Thesis, Stanford, 1971.
(15) I. M. Treitel, Ph.D. Thesis, California Institute of Technology, 1971.
(16) I. M. Treitel, M. F. Flood, R. C. Marsh, and H. B. Gray, *J. Am. Chem. Soc.*, **91**, 6512 (1969).

Glenn M. Tom, Henry Taube*

Department of Chemistry, Stanford University
Stanford, California 94305